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Facile synthesis and replacement reactions of mono-substituted perylene bisimide dyes

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ABSTRACT

Mono-substituted perylene bisimides were synthesized in high yields under mild condition. The starting material was mono-nitrified perylene bisimides instead of usual perylene bisimides halogenated at different levels. Besides phenols and amine, the nucleophilic reagents included alcohol and thiol. The substitution of nitro group was easier and more effective than the substitution of halogen atoms. But the substitution reaction of pyrrolidine afforded mono- and 1,6-disubstituted perylene bisimides owing to the high activity of nitrified perylene bisimides and pyrrolidine. Several replacement reactions between phenols and alcohol based on phenol mono-substituted perylene bisimide were also found. The replacement reactions between phenols was fast and in high yield. The absorption of the mono-substituted perylene bisimides were tunable in the whole visible region.

1. Introduction

Perylene bisimides (PBIs) are important chromospheres in dye chemistry. In light of their diverse and fascinating properties, such as excellent electron acceptor ability, high molar extinction coefficient in the visible region, and high fluorescence quantum yields, PBI dyes represent a classical example of an inherently robust and outstandingly versatile family of organic compounds that have been extensively utilized for a wide range of high technology applications [1–14]. To meet the demands of various applications, the electrochemical and photophysical behavior need to be efficiently tuned by functionalization with hydrophobic, hydrophilic electron-donating or electron-withdrawing groups [15]. The general strategy for introducing groups onto the PBI core was substitution reactions or metal-catalyzed cross-coupling reactions using halogenated PBIs as starting materials. The chlorination or bromination of PBIs could be readily achieved but resulting in a mixture of various PBIs halogenated at different levels. The mixture usually couldn't be separated by column chromatography owing to the bad solubilities as well as the presence of regioisomers. The main products of replacement of the halogen atoms were di- or tetra- substituted symmetrical perylene derivatives [16–20]. Sometimes the mono-substituted derivatives need to be designed for special application. However, neither the halogenation nor the followed replacement of halogen atoms of PBIs was facile to be controlled at the first step [21,22]. In addition, the low activities of halogenated PBIs lead to some reactions are not easy to be carried out. While the nitrification of PBI can be readily controlled at the first step owing to the strong electron-withdrawing effect of nitro group. The mono-nitrated PBI can be achieved under ambient temperature in a high yield of 90%. However, the derivatization method of nitrified PBIs has seldom been investigated. Only a reduction reaction was reported recently to afford amino-substituted PBI [23]. Herein, a serious substitution reaction of mono-nitrified PBI were investigated using different nucleophilic reagents such as phenols, alcohol, thiol and amine. Several replacement reactions based on phenol mono-substituted perylene bisimide between phenols and alcohol were found.

2. Experimental

2.1. Materials

All reagents and solvents were of reagent grade quality. All reagents were obtained from Sinopharm Chemical Reagent Co. Ltd used as received. All organic solvents employed were obtained from Beijing Chemical Corporation. Thin-layer chromatography (TLC) was done on aluminum sheets precoated with Silica 60 F254.

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The purification and isolation of the products were performed by column chromatography on silica gel 60, mesh size 40–63 μm or silica gel 100, mesh size 63–200 μm. *N,N′*-dicyclohexyl-3,4:9,10-tetracarboxylic acid bisimide **1** and *N,N′*-dicyclohexyl-1-nitroperylene-3,4:9,10-tetracarboxylic acid bisimide **2** were synthesized according to the literature procedure [24,25].

2.2. Equipment

^{1}H NMR and ^{13}C NMR were recorded on Bruker 300 MHz or 600 MHz spectrometers in $CDCl_3$ at room temperature. All chemical shifts are quoted relative to TMS ($\delta = 0.0$ ppm); δ values are given in ppm and J values in Hz. Mass spectra were measured on a Bruker Maxis UHR-TOF MS spectrometer. Electronic absorption spectra were measured on a Beijing Purkinje General Instrument Co. Ltd. TU-190 spectrophotometer. The photoluminescence spectra were recorded on a HITACHI FL-4500 spectrofluorometer.

2.3. Synthesis

*2.3.1. Synthesis of N,N′-dicyclohexyl-1-(4-tert-butylphenoxy)-perylene-3,4:9,10-tetracarboxylic acid bisimide (**3**)*

Method a: Compound **2** (200 mg, 0.33 mmol), 4-*tert*-butylphenol (250 mg, 1.67 mmol), 300 mg K_2CO_3 and the catalyzed KI were suspended in 15 mL anhydrous NMP. The reaction mixture was stirred for 6 h at 25 °C under argon atmosphere. Then MeOH (10 mL) and 10% HCl solution (50 mL) were added into the reaction mixture. The precipitate was collected by filtration, washed with methanol, and then dried in vacuum. The crude product was further purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 4:1 to give a dark red solid (210 mg, 90%). Method b: A mixture of *N,N′*-dicyclohexyl-1-(4-formoxylphenoxy)-perylene-3,4:9,10-tetracarboxylic acid bisimide **4** (50 mg, 0.074 mmol) and 4-*tert*-butylphenol (56 mg, 0.37 mmol) in 6 mL anhydrous NMP was stirred for 2 h at 50 °C under argon atmosphere. After being cooled to room temperature, MeOH (10 mL) and water (50 mL) was added into the reaction mixture. The precipitate was collected by filtration, washed with methanol, and then dried in vacuum. The crude product was further purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 4:1 to give **3** (47 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 9.49$ (d, 1H, $J = 8.4$ Hz), 8.60 (m, 5H), 8.24 (s, 1H), 7.48 (d, 2H, $J = 7.8$ Hz), 7.10 (d, 2H, $J = 7.8$ Hz), 5.03 (m, 2H), 2.54 (m, 4H), 1.90 (m, 4H), 1.77 (m, 6H), 1.59–1.46 (m, 6H), 1.39 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 163.48$, 163.30, 162.76, 156.06, 151.83, 148.54, 133.38, 133.30, 132.91, 132.13, 131.28, 130.51, 129.89, 128.87, 128.36, 127.94, 127.71, 127.49, 125.98, 124.89, 124.62, 124.08, 123.46, 123.32, 123.01, 124.31, 123.37, 123.21, 123.12, 122.81, 122.55, 122.03, 121.52, 119.34, 54.58, 54.21, 54.02, 34.55, 31.43, 29.09, 26.59, 25.50. MS (MALDI-TOF): *m/z* = 702.33 (M^+).

*2.3.2. Synthesis of N,N′-dicyclohexyl-1-(4-formaldehyde phenoxy)-perylene-3,4:9,10-tetracarboxylic acid bisimide (**4**)*

Compound **4** was synthesized as the procedure of synthesis of **3**. 100 mg compound **2** and 100 mg 4-hydroxy-benzaldehyde reacted for 6 h in NMP to yield **4** in 92%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 9.99$ (s, 1H), 9.34 (d, 2H, $J = 8.3$ Hz), 8.67 (m, 4H), 8.57 (d, 2H, $J = 8.3$ Hz), 8.27 (s, 1H), 7.96 (d, 2H, $J = 8.6$ Hz), 7.20 (d, 2H, $J = 8.6$ Hz), 5.02 (m, 2H), 2.53 (m, 4H), 1.92 (m, 4H), 1.55–1.28 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 190.39$, 163.64, 163.63, 162.88, 160.11, 153.78, 132.22, 131.84, 128.69, 126.03, 122.71, 118.81, 110.02, 54.01, 53.43, 29.10, 29.07, 26.52, 26.48, 25.42, 25.39. MS (MALDI-TOF): *m/z* = 674.24 (M^+).

*2.3.3. Synthesis of 1-ethoxyl-N,N′-dicyclohexyl perylene-3,4:9, 10-tetracarboxylic diimide (**5**)*

Method a: Compound **2** (100 mg, 0.17 mmol) and 100 mg K_2CO_3 were suspended in 6 mL chloroform and 4 mL ethanol. The mixture was refluxed for 10 h under argon atmosphere. After being cooled to room temperature, the solution was filtrated and evaporated to dryness. The crude product was purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 4:1 to give a red solid **5** (45 mg, 45%). Method b: A mixture of compound **3** (100 mg, 0.14 mmol) and 100 mg K_2CO_3 in 4 mL chloroform and 4 mL ethanol was refluxed for 24 h under argon atmosphere. The solvent was evaporated under reduced pressure to give a solid residue. The crude product was washed with MeOH and then purified by column chromatography on silica gel using CH_2Cl_2/petroleum ether 4:1 as the eluent to afford **5** (28 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 9.45$ (d, 2H, $J = 8.2$ Hz), 8.63–8.16 (m, 6H), 5.04 (m, 2H), 4.51 (m, 2H), 2.59 (m, 5H), 1.94–1.49 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 164.43$, 163.65, 162.96, 132.33, 130.83, 130.04, 127.63, 126.14, 125.37, 124.41, 124.66, 54.79, 54.23, 53.98, 29.11, 26.52, 25.36. MS (MALDI-TOF): *m/z* = 598.25 (M^+).

*2.3.4. Synthesis of 1-propylthio-N,N′-dicyclohexyl perylene-3,4:9,10-tetracarboxylic diimide (**6**)*

Compound **2** (100 mg, 0.17 mmol) and 100 mg K_2CO_3 were suspended in 6 mL chloroform and 4 mL n-propyl mercaptan. The mixture was refluxed for 10 h under argon atmosphere. After being cooled to room temperature, the solution was filtrated and evaporated to dryness. The crude product was further purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 4:1 to give a red solid **6** (37 mg, 35%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 8.82$ (d, 2H, $J = 8.0$ Hz), 8.65–8.60 (m, 3H), 8.55–8.46 (m, 3H), 5.05 (m, 2H), 3.20–3.15 (m, 2H), 2.61–2.57 (m, 5H), 1.96–1.93 (m, 4H), 1.83–1.75 (m, 6H), 1.52–1.38 (m, 8H), 1.09–1.04 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 163.59$, 163.54, 163.43, 139.52, 133.72, 133.41, 132.82, 131.98, 131.03, 130.41, 130.26, 129.21, 128.88, 128.42, 127.29, 126.52, 125.99, 123.19, 123.07, 122.75, 122.02, 121.95, 54.19, 54.03, 37.95, 30.84, 29.15, 26.58, 25.48, 21.92, 13.54. MS (MALDI-TOF): *m/z* = 628.24 (M^+).

*2.3.5. Synthesis of 1-pyrrolidinyl-N,N′-dicyclohexyl perylene-3,4:9,10-tetracarboxylic diimide (**7**a) and 1,6-dipyrrolidinyl-N,N′-dicyclohexyl perylene-3,4:9,10-tetracarboxylic diimide (**7**b)*

Compound **2** (100 mg, 0.17 mmol) in 5 mL pyrrolidine was stirred at 0 °C for 5 h under argon atmosphere. After the solvent being evaporated, the solid was purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 2:1 to give blue solid **7**a (32 mg, 30%) and blue-green solid **7**b (24 mg, 20%). **7**a: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 8.64$ (d, 2H, $J = 8.0$ Hz), 8.47–8.52 (m, 4H), 7.53 (d, 2H, $J = 8.0$ Hz), 5.09 (m, 2H), 3.79 (m, 2H), 2.79 (m, 2H), 2.65–2.57 (m, 4H), 2.13 (m, 2H), 1.96–1.92 (m, 4H), 1.81–1.78 (m, 6H), 1.52–1.38 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 164.31$, 164.24, 164.13, 148.42, 135.19, 134.93, 132.51, 130.90, 130.65, 128.94, 127.07, 126.58, 124.18, 123.57, 123.11, 122.83, 122.57, 122.14, 120.38, 119.53, 115.96, 53.99, 53.75, 52.24, 29.68, 29.18, 29.10, 26.60, 25.72, 25.50. MS (MALDI-TOF): *m/z* = 623.28 (M^+). **7**b: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 8.65$ (d, 2H, $J = 8.0$ Hz), 8.33 (s, 2H), 7.90 (d, 2H, $J = 8.0$ Hz), 5.13–5.04 (m, 2H), 3.71 (m, 4H), 2.67–2.56 (m, 8H), 2.01–1.90 (m, 12H), 1.76 (m, 6H), 1.27–1.51 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 160.10$, 159.85, 145.27, 130.76, 126.26, 125.40, 123.70, 123.55, 118.60, 118.56, 113.62, 112.85, 112.46, 112.22, 49.20, 48.80, 47.30, 24.48, 24.38, 21.89, 21.83, 20.87. MS (MALDI-TOF): *m/z* = 692.34 (M+).

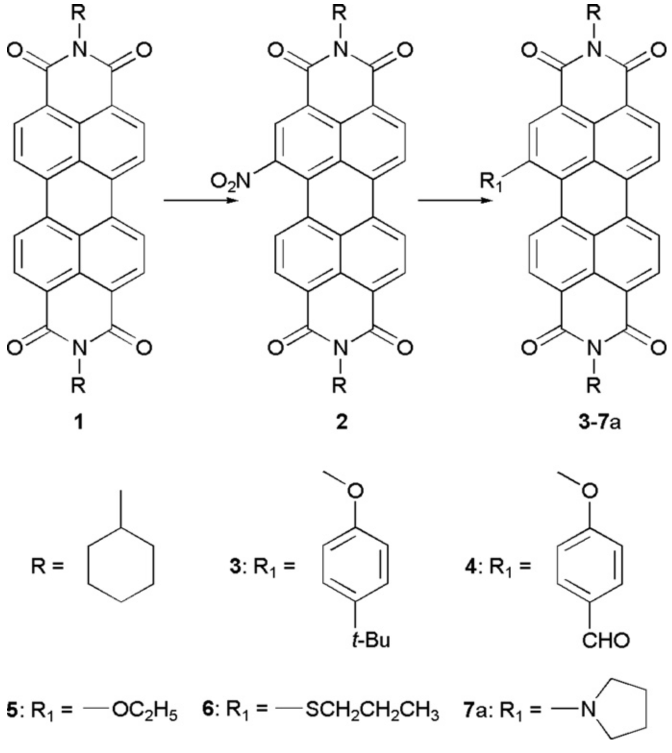
3. Results and discussions

3.1. Synthesis

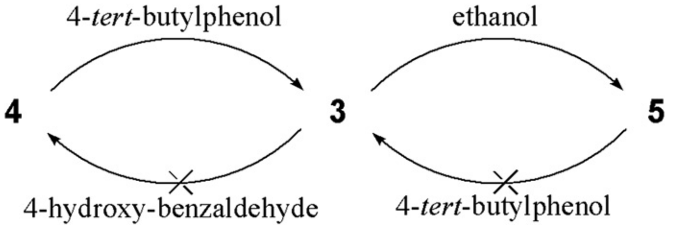
The chemical structures of compounds **1**-**7**a and their synthetic routes are shown in Scheme 1. The synthesis started from an imidization of perylene bisanhydride by reaction with cyclohexylamine. The mono-nitrated perylene-3,4:9,10-tetracarboxylic bisimide **2** was achieved by a reaction of perylene bisimides **1** with cerium (IV) ammonium nitrate (CAN) and HNO_3 under ambient temperature in a high yield. The substitutions of nitro group of **2** with 4-*tert*-butylphenoxy, ethoxyl, propylthio and pyrrolidinyl group were performed in different solvents to obtain the corresponding substituted products **3**-**7**. By exchange of phenols or ethanol, compound **3** could be prepared from compound **4** and could also be used to prepare compound **5**. The replacement reactions are summarized in Scheme 2.

1-nitro-*N,N′*-dicyclohexyl perylene-3,4:9,10-tetracarboxylic bisi mide **2** was synthesized by the reaction of *N,N′*-dicyclohexyl perylene-3,4:9,10-tetracarboxylic bisimide with 96% nitric acid and $Ce(NH_4)_2(NO_3)_6$ in CH_2Cl_2 with a high yield of more than 90%. Usually, the bromination of perylene bisimide **1** resulted in main products of regioisomers of dibrominated PBIs and low ratio of mono- as well as tri-brominated PBIs. Compared with the bromination of PBIs, the nitrification of PBI was readily to be controlled at first step due to the far stronger electron-withdrawing effect of nitro group than bromine atom. In addition, the mono-nitrified PBI has a good solubility in organic solvent thus its purification is easy.

The substitution reactions of nitrified PBI could be carried out smoothly with phenols in high yields. The yields of substitution reactions of compound **2** with 4-*tert*-butylphenol in different solvents were compared. The reaction proceeded entirely in *N*-methyl-2-pyrrolidone (NMP) with a yield of ca 90%. However, in DMF or $CHCl_3$, the yields of the reactions under the same condition were less than 65%. Compared with the similar reaction of mono-bromized PBI reacting over 100°C [26], the substitution of nitro group by 4-*tert*-butylphenoxy group took place quickly at room temperature. Catalyzed by KI, the reaction time could be shortened from 10 h to 6 h. Almost without any byproduct, the product was pure enough to be used in other reactions just through precipitation from the resulting solution by adding methanol and HCl solution and then being washed with methanol. Compound **4** was synthesized as the procedure of synthesis of **3** using 4-hydroxybenzaldehyde as phenol. Besides phenols, alcohol and thiol could react with mono-nitrified PBI in chloroform to yield corresponding substituted products. This kind of reaction has seldom been reported for halogenated PBI owing to its lower activity than nitrified PBI [27].



Scheme 1. The synthesis of compounds **3**-**7**a.



Scheme 2. The replacement reactions between **3**, **4**, **5**.

Generally the substitution reaction of bromized PBIs with pyrrolidine take place at original position, i.e. the bromine atoms are replaced by pyrrolidinyl groups [23,28,29]. Similar as the bromized PBIs, mono-nitrified PBI **2** could react with pyrrolidine. But beside the mono-substituted product of **7**a, 1,6-disubstituted PBI **7**b was also obtained. When the reaction was carried out under 25 °C, **7**a was the major product. Otherwise **7**b was the major product.

Besides the substitution reactions of halogenated or nitrified PBIs, the replacement reactions of phenol substituted PBIs were noted. Compound **4** could react with 4-tert-butylphenol in NMP to give compound **3** in high yield. However compound **4** couldn't be prepared from **3**. Similarly compound **3** could react with ethanol in chloroform to give compound **5**. But compound **3** couldn't be prepared from **5**. A reaction mechanism of those replacement reactions was proposed that a weaker nucleophile could be substituted by a stronger nucleophile to form new O—C bond.

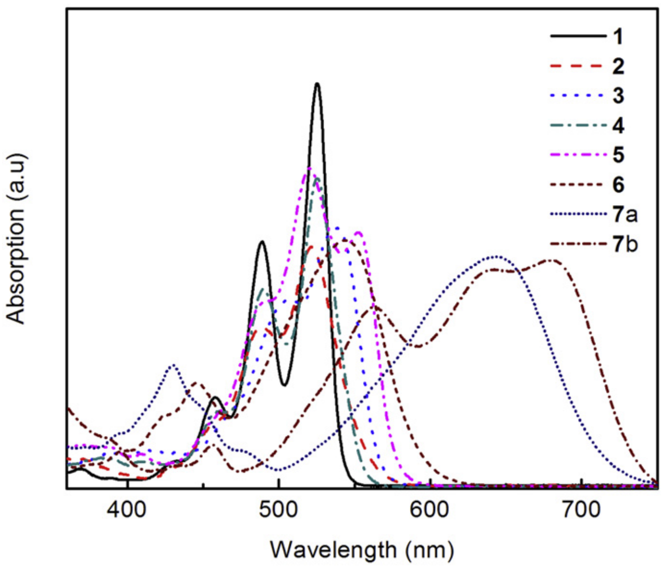


Fig. 1. Absorption spectra of compound **1**-**7** in chloroform (10^{-5} M).

Table 1
Absorption data for **1**-**7** in chloroform (10^{-5} M).

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**a	**7**b
λ_{max} (nm)	525.5	521.5	538.5	525.5	520.5	545.5	644.0	682.0
ε (10^4 M^{-1} cm^{-1})	7.87	3.10	3.47	4.11	4.26	3.29	3.13	3.16

3.2. *Absorption properties of dyes*

The UV–vis absorption spectra of the compounds in chloroform at room temperature are shown in Fig. 1 and the absorption data are given in Table 1. All of the compounds show intense absorption in the visible region. Compound **1** shows strong PBI core absorption band at 526 nm. Compared with compound **1**, a slight blue-shift about 4 nm in the absorption of **2** is observed. The phenomenon may be attributed to the decrease of molecular rigidity due to the enhanced steric hindrance induced by the nitro group. The maximal absorption bands of compound **3** and **4** red-shift about 17 and 4 nm respectively compared with that of **2**. Because the introduction of phenoxy group at the bay position has enlarged the conjugation system of PBI core. The longest wavelength absorption band of **5** and **6** appear at 553 and 544 nm respectively. Notably, introduction of electron-donating groups of pyrrolidinyl groups induces remarkable red-shifts and the pyrrolidinyl-substituted compounds **7**a and **7**b display large differences in their absorptive features compared with **2**. The maximum absorption of **7**a appears at 643 nm. The lowest energy band is highly red-shifted with respect that of nitro-substituted PBI **2**, reflecting pronounced electronic interaction between PBI core and pyrrolidinyl groups. In addition, it also exhibits a higher energy electronic transition at 430 nm. Compared with compound **7**a, the lowest energy band has a longer red-shift about 38 nm for **7**b. In addition, a shoulder peak shows as strong as the maximal absorption band and an additional strong band appears at 563 nm. Due to the compound **7**a and **7**b cover a large region of the visible light, the compounds may be used as special dyes in solar cell.

3.3. *Fluorescence properties of dyes*

The fluorescence spectra of compounds **1**, **3**, **4**, **5** and **6** were investigated at room temperature. As shown in Fig. 2, the maximum emission band of **1**, **3**, 5 and **6** locate at 534, 564, 574 and 634 nm. Compared with strong emission of phenol substituted compounds **3** and **4**, alkyl substituted compounds **5** and **6** show weaker emission. Incorporated with strong electron-withdrawing group of nitryl and electron-donating groups of pyrrolidinyl, compound **2**, **7**a and **7**b exhibit very weak emission.

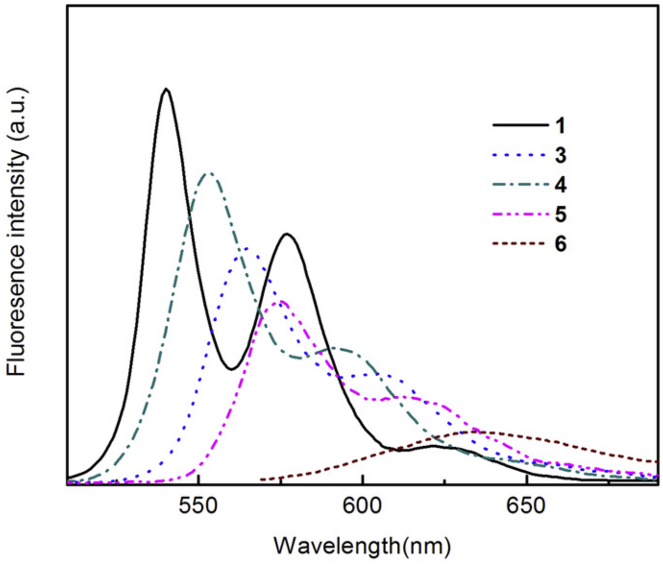


Fig. 2. Fluorescence spectra of compound **1**, **3**, **4**, **5** and **6** in chloroform (10^{-5} M).

4. Conclusions

In conclusion, the substitution reactions of mono-nitrified perylene bisimides have been investigated. Besides phenols, alcohol and thiol could carry out the substitution reaction. For pyrrolidine, both mono and 1,6-disubstituted PBIs were obtained. The pyrrolidinyl substituted PBIs show intense and broad absorption in the visible region. In addition, several replacement reactions between phenols and alcohol based on phenol mono-substituted perylene bisimide have been developed.

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References

[1] Jones BA, Ahrens MJ, Yoon MH, Facchetti A, Marks TJ, Wasielewski MR. High-mobility air-stable n-type semiconductors with processing versatility: dicyanoperylene-3,4:9,10-bis(dicarboximides). Angew Chem Int Ed 2004;43:6363–6.
[2] Guo XF, Zhang DQ, Zhu DB. Logic control of the fluorescence of a new dyad, spiropyran-perylene diimide-spiropyran, with light, ferric ion, and proton: construction of a new three-input “AND” logic gate. Adv Mater 2004;16:125–30.
[3] Tian H, Liu PH, Zhu WH, Gao EQ, Wu DJ, Cai SM. Synthesis of novel multichromophoric soluble perylene derivatives and their photosensitizing properties with wide spectral response for SnO_2 nanoporous electrode. J Mater Chem 2000;10:2708–15.
[4] Ranke P, Bleyl I, Simmerer J, Haarer D, Bacher A, Schmidt HW. Electroluminescence and electron transport in a perylene dye. Appl Phys Lett 1997;71:1332–4.
[5] Schmidt-Mende L, Fechtenkotter A, Müllen K, Moons E, Friend RH, MacKenzie JD. Self-organized discotic liquid crystals for high-efficiency organic photovoltaics. Science 2001;293:1119–22.
[6] O’Neil MP, Niemczyk MP, Svec WA, Gosztola D, Gaines GL, Wasielewski MR. Picosecond optical switching based on biphotonic excitation of an electron donor-acceptor-donor molecule. Science 1992;257:63–5.
[7] Baffreau J, Leroy-Lhez S, Anh NV, Williams RM, Hudhomme P. Fullerene C_{60}-perylene-3,4:9,10-bis(dicarboximide) light-harvesting dyads: spacer-length and bay-substituent effects on intramolecular singlet and triplet energy transfer. Chem Eur J 2008;14:4974–92.
[8] He XR, Liu HB, Li YL, Wang S, Li YJ, Wang N, et al. Gold nanoparticle-based fluorometric and colorimetric sensing of copper(II) ions. Adv Mater 2005;17:2811–5.
[9] Zhao YJ, Zhang X, Li DQ, Liu DC, Jiang WF, Han CX, et al. Water-soluble 3,4:9,10-perylene tetracarboxylic ammonium as a high-performance fluorochrome for living cells staining. Luminescence 2009;24:140–3.
[10] Würthner F. Perylene bisimide dyes as versatile building blocks for functional supramolecular architectures. Chem Commun 2004;14:1564–79.
[11] Huang C, Barlow S, Marder SR. Perylene-3,4:9,10-tetracarboxylic acid diimides: synthesis, physical properties, and use in organic electronics. J Org Chem 2011;76:2386–407.
[12] Li C, Wonneberger H. Perylene imides for organic photovoltaics: yesterday, today, and tomorrow. Adv Mater 2012;24:613–36.
[13] Lu XY, Guo ZQ, Sun CY, Tian H, Zhu WH. Helical assembly induced by hydrogen bonding from chiral carboxylic acids based on perylene bisimides. J Phys Chem B 2011;115:10871–6.
[14] Tan WJ, Li X, Zhang JJ, Tian H. A photochromic diarylethene dyad based on perylene diimide. Dyes Pigm 2011;89:260–5.
[15] Grimsdale AC, Müllen K. The chemistry of organic nanomaterials. Angew Chem Int Ed 2005;44:5592–629.

[16] Würthner F, Osswald P, Schmidt R, Kaiser TE, Mansikkamaki H, Könemann M. Synthesis and optical and electrochemical properties of core-fluorinated perylene bisimides. Org Lett 2006;8:3765–8.

[17] Ahrens MJ, Sinks LE, Rybtchinski B, Liu W, Jones BA, Giaimo JM, et al. Self-Assembly of supramolecular light-harvesting arrays from covalent multi-chromophore perylene-3,4:9,10-bis(dicarboximide) building blocks. J Am Chem Soc 2004;126:8284–94.

[18] Liu Y, Xiao SQ, Li HM, Li YL, Liu HB, Lu FS, et al. Self-Assembly and characterization of a novel hydrogen-bonded nanostructure. J Phys Chem B 2004; 108:6256–60.

[19] Yuan ZY, Xiao Y, Li Z, Qian XH. Efficient synthesis of regioisomerically pure bis(trifluoromethyl)-substituted-3,4:9,10-perylene tetracarboxylic bis(benzimidazole). Org Lett 2009;11:2808–11.

[20] Rajasingh P, Cohen R, Shirman E, Linda J, Shimon W, Rybtchinski B. Selective bromination of perylene diimides under mild conditions. J Org Chem 2007;72: 5973–9.

[21] Alvino A, Franceschin M, Cefaro C, Borioni S, Ortaggi G, Bianco A. Synthesis and spectroscopic properties of highly water-soluble perylene derivatives. Tetrahedron 2007;63:7858–65.

[22] Fan LQ, Xu YP, Tian H. 1,6-Disubstituted perylene bisimides: concise synthesis and characterization as near-infrared fluorescent dyes. Tetrahedron Lett 2005;46:4443–7.

[23] Chen KY, Fang TC, Chang MJ. Synthesis, photophysical and electrochemical properties of 1-aminoperylene bisimides. Dyes Pigm 2011;92:517–23.

[24] Ma YS, Wang CH, Zhao YJ, Yu Y, Han CX, Qiu XJ, et al. Perylene diimide dyes aggregates: optical properties and packing behavior in solution and solid state. Supramol Chem 2007;19:141–9.

[25] Chen KY, Chow TJ. 1,7-Dinitroperylene bisimides: facile synthesis and characterization as n-type organic semiconductors. Tetrahedron Lett 2010;51: 5959–63.

[26] Choi J, Sakong C, Choi JH, Yoon C, Kim JP. Synthesis and characterization of some perylene dyes for dye-based LCD color filters. Dyes Pigm 2011;90: 82–8.

[27] Zhao CT, Zhang YX, Li RJ, Li XY, Jiang JZ. Di(alkoxy)- and di(alkylthio)-substituted perylene-3,4;9,10-tetracarboxy diimides with tunable electrochemical and photophysical properties. J Org Chem 2007;72: 2402–10.

[28] Shibano Y, Umeyama T, Matano Y, Imahori Hiroshi. Electron-donating perylene-tetracarbo- xylic acids for dye-sensitized solar cells. Org Lett 2007;9: 1971–4.

[29] Dubey RK, Efimov A, Lemmetyinen H. 1,7- and 1,6-regioisomers of diphenoxy and dipyrrolidinyl substituted perylene diimides: synthesis, separation, characterization, and comparison of electrochemical and optical properties. Chem Mater 2011;23:778–88.